

Synergistic Flame Retardant Effect of Cerium Oxide in Ethylene-Vinyl Acetate/Aluminum Hydroxide Blends

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ABSTRACT: The flammability characterization and synergistic flame retardant effect of cerium oxide (CeO_2) in the ethylene-vinyl acetate/aluminum hydroxide blends were studied using limiting oxygen index (LOI), UL-94 test, and cone calorimeter test (CCT). The results showed that the addition of a given amount of CeO_2 apparently increased the LOI value and UL-94 rating. The data

obtained from the CCT indicated that the addition of CeO_2 greatly decreased the heat release rate and prolonged the combustion time. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1889–1893, 2010

Key words: cerium oxide; aluminum hydroxide; synergistic effect; flame retardant

INTRODUCTION

Ethylene-vinyl acetate (EVA) copolymers with different acetate contents are extensively used in many fields, especially in the cable industry as excellent insulating materials with good physical and mechanical properties.¹ However, EVA copolymers are particularly flammable and emit a large amount of smoke as burning, which restrict their practical applications. Therefore, it is very important to improve the flame retardance in the applications of EVA materials.

In recent years, developing halogen-free flame retardant polymeric materials has become a prominent trend. Many investigations have demonstrated that aluminum hydroxide (ATH) is a nontoxic and smoke suppressing halogen-free flame retardant additive in flame retardant polymeric materials. However, ATH has an essential disadvantage that more than 60% ATH loading is required to meet flame retardant properties, which could be detrimental to the mechanical properties of flame retardant materials. Many investigations have been done on ATH incorporated with other halogen-free flame retardant synergistic agent^{2–9} to enhance the flame resistance and decrease its high loading level of ATH. Ramazani et al. reported the synergistic effect

of zinc borate with ATH in flame retardance and physical–mechanical properties of propylene composites.³ Schartel et al. studied the flame retardant effect of phosphonium-modified layered silicate with ATH in epoxy resins nanocomposites.⁶

Rare earth oxides, such as lanthanum oxide (La_2O_3), can be used as synergistic additives in intumescent flame retardant systems. Li et al. have reported the synergistic effects of lanthanum oxide on a novel intumescent flame retardant polypropylene system.¹⁰ Wu et al. have reported the synergistic effect of lanthanum oxide on intumescent flame-retardant polypropylene-based formulations.¹¹ Very recently, our group has found La_2O_3 has synergistic flame retardant effect with ATH in EVA/ATH/ La_2O_3 composites.¹² As far as we are aware, however, no work has been done on the synergistic effect of cerium oxide (CeO_2) in EVA/ATH blends. This work is mainly devoted to report the investigation of the flammability characterization and synergistic mechanism of CeO_2 with ATH in the EVA/ATH blends using limiting oxygen index (LOI), UL-94 test, and cone calorimeter test (CCT).

EXPERIMENTAL

Materials

EVA28 (containing 28 wt % vinyl acetate) was bought from Sumitomo Chemical Co., (Japan). ATH, with decomposition temperature of about 220°C and average particle size of about 2.0 μm , was supplied by Martin Corp., Germany. CeO_2 with an average particle size of 3.0 μm was obtained from Rare Earth Hi-Tech (China). The formulations are given in Table I.

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TABLE I
The Results of LOI and UL-94 Test of EVA/ATH/CeO₂ Compositions

Sample code	EVA/%	ATH/%	CeO ₂ /%	LOI	UL-94
EVA-0	100.0	–	–	17.0	No rating, dripping
EVA-1	45.0	55.0	–	35.2	No rating, dripping
EVA-2	45.0	54.0	1.0	37.0	No rating, no dripping
EVA-3	45.0	53.5	1.5	38.0	No rating, no dripping
EVA-4	45.0	53.0	2	37.6	No rating, no dripping
EVA-5	45.0	52.5	2.5	37.0	No rating, no dripping

Sample preparation

All the samples were prepared by using a mixer with the same procedures. EVA was added into the mixer with rotational speed of 20 rpm at 120°C. ATH filler and CeO₂ were added after EVA polymer was melted and the mixing was carried out at 50 rpm for 10 min. The obtained composites were finally compression molded at 120°C for 10 min under 10 MPa into sheets of suitable thickness. Samples for testing were cut from the compressed sheets according to the standards mentioned in the following part.

Measurements

Limiting oxygen index

LOI was measured according to ASTM D 2863. The apparatus used was an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China). The specimens used for the test were of dimensions 100 × 6.5 × 3 mm³.

UL-94 test

The vertical test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China) according to the UL-94 test standard. The specimens used were of dimensions 100 × 13 × 3 mm³.

Cone calorimeter test

The cone calorimeter (Stanton Redcroft, UK) tests were performed according to ISO 5660 standard procedures. Each specimen of dimensions 100 × 100 × 4 mm³ was wrapped in aluminum foil and exposed horizontally to an external heat flux of 50 kW/m².

RESULTS AND DISCUSSION

LOI and UL-94 rating

The LOI and UL-94 tests are widely used to evaluate flame retardant properties of materials and to screen flame retardant formulations. Table I presents the LOI values and UL-94 testing results of the flame

retarded EVA composites. It can be seen from Table I that the LOI value of sample EVA-1 containing 55 wt % ATH increases rapidly from 17.0 to 35.2 of original EVA sample EVA-0 without any additive. The LOI values of samples (EVA-1 to EVA-3) gradually increase to 38.0 with increase in the loading of CeO₂ in the formulation. However, the LOI value of sample EVA-5 decreases to 37.0 when the loading of CeO₂ reaches to 2.5 wt %. However, samples EVA-2 with 54.0 wt % ATH and 1.0 wt % CeO₂ have no dripping phenomenon in the UL-94 test. With further increasing the content of CeO₂ even to 2.5 wt %, samples EVA-5 cannot pass the V-0 rating. These results indicate that the addition of a suitable amount of CeO₂ can increase the flame retardance of EVA/ATH blends. The above phenomena can be illustrated that the addition of CeO₂ increases the polymer melting viscosity, which favors the LOI and UL-94 test.¹³

Cone calorimeter study

Heat release rate (HRR)

Although the LOI and UL-94 tests are widely used to evaluate the flame retardation of materials, especially for screening flame retarded formulations of polymers, the cone calorimeter provides a wealth of information on the combustion behavior.¹⁴ Some cone calorimeter results have been found to correlate well with those obtained from large-scale fire tests and can be used to predict the behavior of materials in real fires.¹⁵ For example, the peak heat release rate (HRR) is an important parameter, which can be used to evaluate the intensity of fires.¹⁶

Fire performance of flame retardant EVA composites was tested using cone calorimeter. It can be found from Figure 1 that the HRR curves of the flame retardant EVA composites obtained from the CCT and that pure EVA (EVA-0) burns very fast after ignition. A very sharp HRR curve appears at the range of 30–240 s, whereas sample EVA-1 with 55.0 wt % ATH shows a dramatic decline of the HRR curve and its combustion is prolonged from 240 to 480 s of the control sample EVA-0. EVA-2 with 1 wt % CeO₂ shows its combustion is prolonged from 480 to 520 s of the control EVA-1.

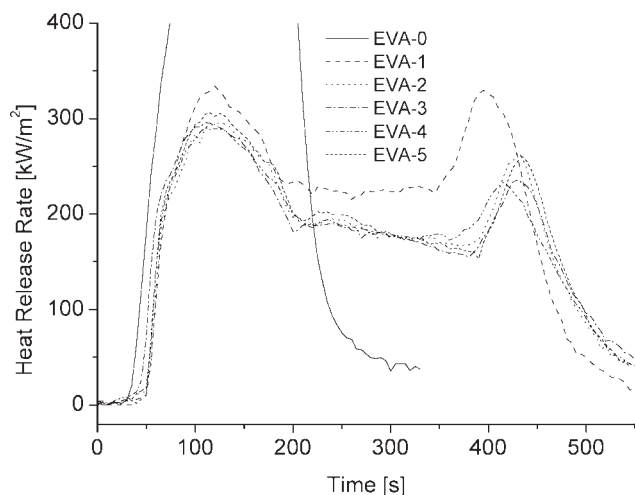


Figure 1 The HRR curves of EVA/ATH/CeO₂.

With the addition of CeO₂, the burning time is prolonged.

When comparing the HRR curve of EVA-2 with that of EVA-1, incorporation of 1 wt % CeO₂ into EVA/ATH blends makes a decrease of HRR. To our surprise, a further reduction of the second PHRR (curve EVA-3 to EVA-4) was obtained when the same amount of ATH premixed with CeO₂ content increasing. The HRR of samples (EVA-1 to EVA-5) shows two separate peaks during burning, which indicates the gradual burning of the specimen through the thickness after the initial charred layers were formed. This combustion feature of multiple HRR peaks has also been reported by Grexa and Le Bras.^{17,18} The first PHRR of the flame retardant samples (EVA-1 to EVA-4) decrease with increasing loading of CeO₂. Then, the first PHRR of sample EVA-5 increases than other samples with addition of CeO₂. In the case of the second PHRR of the flame retardant series, the same trend can be found in Figure 1, and the reduction of PHRR is more obvious than that of the first ones. The above phenomena indicate that CeO₂ contributes to decrease the flammability of materials. CeO₂ did not act as a component which accelerates the burning of EVA, but as a synergistic retardant of ATH to reduce the burning rate of EVA. It can be found that the HRR of EVA-3 and EVA-4 is the lowest, which indicate the incorporation of CeO₂ into the ATH flame retardant system can help to improve the flame retardancy of EVA. It is important to find out the reason that the CeO₂ could improve the flame retardancy of EVA/ATH composites.

CeO₂ is usually considered to be an inert additive in flame retardant systems, but to be a catalyst of gas combustion.¹⁹ However, the above data indicate that the flame retardant performances of EVA/ATH blends are enhanced by partly substituting ATH

with CeO₂. The mechanism of the reduction in HRR is mainly due to the physical processes and chemical process in the condensed phase, as reported in the literature.^{10,11} CeO₂ tends to accumulate near the regressing sample surface without sinking through the polymer melt layer during the gasification/burning process.^{20,21} The accumulated CeO₂ consequently formed a charred layer by collaborating with Al₂O₃ from the decomposition of ATH, which acts as a heat insulation barrier (Fig. 2). This charred layer prevented heat transfer and transportation of degraded products between melting polymer and surface, thus reduced the HRR and related parameters.

Char residue

Figure 2 shows the weight of the char residues. During combustion, a compact char may occur on the surface of the burning creating a physical protective barrier on the surface of material. The physical process of the char would act as a protective barrier in addition to the compact shield and can thus limit the oxygen diffusion to the substrate or give a less disturbing low volatilization rate. In this study, it was found that the compact char residue of EVA1-EVA5 formed on the surface of the sample. The effect of the heat insulation barrier becomes excellent with the addition of CeO₂.

Total heat release (THR)

Figure 3 presents the THR for all the samples. The slope of THR curve can be assumed as representative of fire spread.²² From Figure 3, it can be seen that the THR is decreased by the addition of CeO₂. It is very clear that the flame spread of samples (EVA-0 to EVA-5) has decreased, and the flame spread of sample EVA-3 and EVA-4 is

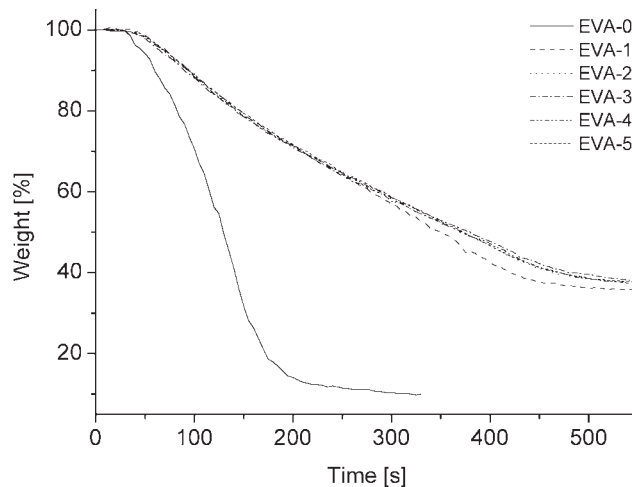


Figure 2 The Mass curves of EVA/ATH/CeO₂.

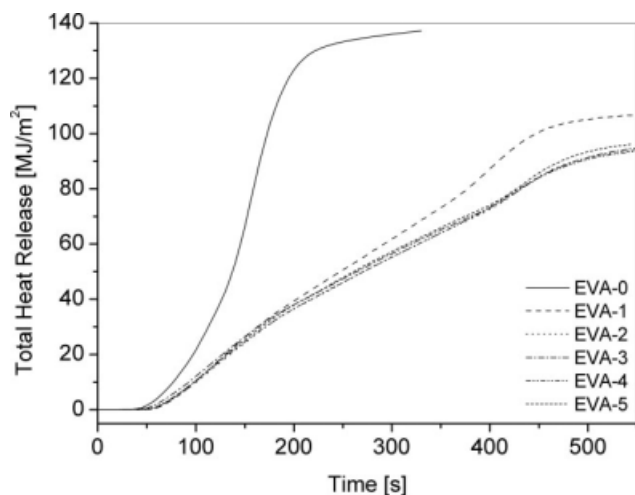


Figure 3 The THR curves of EVA/ATH/CeO₂.

comparatively the lowest. This phenomena can also be explained that the migration of CeO₂ onto the surface of the sample, which can barrier from the flame zone to the underlying materials, and restrain the flammable gases to flame zone. Another important reason may be that CeO₂ can capture free radicals from the decomposition of EVA.^{23,24} It is also suggested there is a synergistic effect of flame retardance between ATH and CeO₂.

Digital photos of residues

Figure 4 are digital photos of residues of EVA/ATH/CeO₂ series. It can be seen that the residue on

the surface of sample EVA-1 without CeO₂ is very loose; however, a coherent residue can be formed on the surface of the sample with CeO₂. Furthermore, for EVA/ATH/CeO₂ series, there is less char formed on the surface of the sample with the addition of CeO₂, as shown in Figure 4. The reason may be that CeO₂ can migrate onto the surface of the sample. On the one hand, the aggregated CeO₂ has the effect of isolating oxygen transferring. On the other hand, CeO₂ can interact with Al₂O₃ from the decomposition of ATH to form some ceramic material.²⁵ The above two aspects help to improve the flame retardancy of the composites. From the char structure, we can explain the combustion phenomenon of the flame retardant EVA composites. The formation of the efficient ceramic material can prevent the heat mass transfer between the flame zone and the burning substrate, and thus protect the underlying materials from further burning and retard the pyrolysis of polymers. It can be illustrated that the mass increases with the addition of CeO₂ from 250 to 550 s (Fig. 2). As a result, HRR values are reduced, as shown in Figure 1.

CONCLUSIONS

It has been found that CeO₂ can have a synergistic effect on flame retardancy with ATH in EVA/ATH/CeO₂ blends. A suitable amount of CeO₂ can increase the LOI value and UL-94 rating. The optimum amount of CeO₂ in the blends is 1.5 wt %. The synergistic mechanism of CeO₂ with ATH is mainly

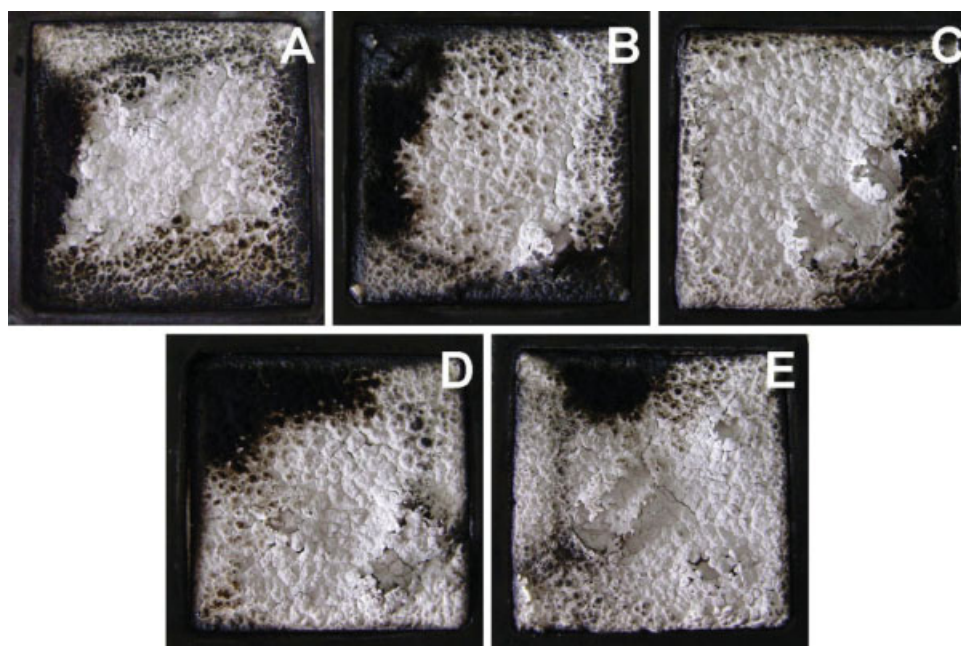


Figure 4 Photographs after cone calorimeter test: (A) EVA-1, (B) EVA-2, (C) EVA-3, (D) EVA-4, and (E) EVA-5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

due to its physical effect in the condensed phase, as revealed by CCT data showing that addition of CeO₂ can lead to the formation of a more thermally stable barrier, and the residual char of the system with CeO₂ is higher than that of the system without CeO₂. A more compact barrier produced by CeO₂ collaborating with ATH consequently leads to the decrease of HRR, Mass, and THR as detected by CCT.

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